

PM_{2.5} SEMI-VOLATILE MATERIAL: PHILADELPHIA AND ATLANTA SUPERSITE RESULTS

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ABSTRACT

Ammonium nitrate and semi-volatile organic material are significant components of fine particulate material in most urban atmospheres which are not properly identified during sampling with single filter samplers because of the loss of these materials from the collected particles during sampling. The composition of fine particulate material at the Philadelphia NARSTO and Atlanta Supersite studies was measured with two PC-BOSS diffusion denuder samplers and with a RAMS continuous monitor. Samples collected with the PC-BOSS were analyzed for sulfate, nitrate (including ammonium nitrate lost from collected particles during sampling), soot, organic material (including semi-volatile organic material lost from particles during sampling), crustal material, and mass. Significant amounts of semi-volatile organic material were present in the particles throughout both studies and semi-volatile organic material was not well measured with single filter samplers such as the a TEOM monitor or the PM_{2.5} FRM.

BACKGROUND

Human health endpoints associated with exposure to airborne particulate matter (PM) include increased mortality and morbidity from respiratory and cardiopulmonary disease^{1,2}. These effects are observed with exposure to concentrations substantially below the U.S. PM₁₀ ambient air quality standard. The observed exacerbation of health problems is believed to be associated more closely with exposure to fine particles than coarse particles. As a result, the U.S. Environmental Protection Agency has promulgated³ revised standards for PM, which establishes new annual and 24-hour fine particle standards with PM_{2.5} as the indicator. This recognition of fine and coarse particles as different classes of PM pollutants is an advance in the understanding and control of PM. However, ambient fine particulate matter is not a single pollutant, but a mixture of many chemical species. Major components include: sulfate, nitrate, ammonium, and hydrogen ions; trace elements (including toxic metals); organic material; elemental carbon (or soot); crustal components; and water. Stable species such as trace and crustal elements, and sulfate can be accurately measured by available technology. However, monitoring technologies for organic carbon, nitrate and particulate water are not as well established.

The collection of particulate matter containing ammonium nitrate on a filter results in displacement of the equilibrium, $\text{NH}_4\text{NO}_3 \cdot x\text{H}_2\text{O}(s) = \text{HNO}_3(g) + \text{NH}_3(g) + x\text{H}_2\text{O}(g)$, with the extent of loss of ammonium nitrate from particles being a function of sampling time, filter face velocity, composition of the fine particles being sampled, temperature, humidity and other factors. However, in the eastern United States there tends to be little nitrate in fine particles because of the high acidity of the aerosol.

A second fine particulate component for which significant losses during sampling on a filter have been documented is semi-volatile organic material. Preliminary studies in eastern sites have indicated that an average of about one-half of fine particulate organic material is lost due to the stripping of semi-volatile organic compounds from the particles during sampling. The hypothesis of the studies reported here is that fine particulate mass will be significantly under-determined in eastern urban environments using the proposed PM_{2.5} Federal Reference Method (FRM) because of the loss of semi-volatile material from the particles during sampling. It is postulated that fine particulate mass, including the semi-volatile fine particulate species, is an appropriate surrogate for the components of fine particles which have been associated with observed mortality and morbidity effects in epidemiological studies. Under-determination of these semi-volatile species will tend to over emphasize the importance of non-volatile fine particulate components such as sulfate. In addition, the need is recognized for both real-time and week-long sampling methods which accurately measure PM_{2.5}, including the volatile constituents ammonium nitrate and semi-volatile organic material. The studies reported here used a PC-BOSS diffusion denuder sampler for the determination and characterization of fine particulate

mass, including semi-volatile organic and nitrate species which can be lost from fine particles during sampling with a filter, and a RAMS for the continuous measurement of fine particles.

EXPERIMENTAL

Samples were collected at the NARSTO summer 1999 sampling site at the Baxter Water Treatment Plant in Philadelphia PA during July, and at the EPA Supersite program at the Georgia Power facility in Atlanta GA during August. The two diffusion denuder samplers intercompared in these two studies were:

1. PC-BOSS

The combination of the technology used in the BIG BOSS sampling system⁴ and the Harvard particle concentrator has resulted in the Particle Concentrator-Brigham Young University Organic Sample System⁵. The system has been optimized to meet the following criteria; 1. Removal of at least 75% of the gas phase material before the sampled aerosol is passed through the diffusion denuder. 2. Efficiency >99% for the removal of SO₂, HNO₃, and gas phase semi-volatile organic material in the minor flow. 3. Determination of particulate mass, carbonaceous material and nitrate with a diffusion denuder sampler.

The inlet to the sampler is a Bendix cyclone with a particle cut of 2.3 μm aerodynamic diameter at an inlet flow of 150 L/min. The cyclone is followed by a virtual impactor particle concentrator. The particle concentrator separates most of the gas phase material into the major flow and leaves particles larger than the cut point (about 0.1 μm) along with a significantly reduced fraction of the gas phase material in the minor flow. The minor flow (25% of the total 150 L/min flow) containing concentrated particles enters the BOSS diffusion denuder^{4,6}. The denuder is comprised of 17 (4.5 x 58 cm) strips of Schleicher and Schuell charcoal impregnated filter paper which are separated at the long edges by 2-mm glass rods. This gives a diffusion denuder with both high efficiency and high capacity. The denuder is followed by two parallel filter packs. The filter pack containing a 47 mm quartz filter (Pallflex, pre-fired) followed by a 47 mm charcoal impregnated filter (3M EMPORE Carbon) is used to determine fine particulate nitrate and carbonaceous material, including semi-volatile organic material lost from the particles during sampling. The second filter pack contains 47 mm Teflon (Gelman Teflo) and nylon (Gelman Nylasorb) filters to determine mass, acidity, ammonium ion, sulfate and nitrate, including any nitrate lost from particles during sampling.

2. RAMS

The RAMS (Real-time Ambient Mass Sampler) is based on the modification of a TEOM monitor to allow for the determination of fine particle mass, including the volatile species⁷. Gas phase compounds which can be absorbed by a charcoal impregnated filter (CIF) are removed by a series of denuders and a Nafion dryer. The resulting airstream is then sampled by a TEOM monitor with a "sandwich" filter containing an R&P TX40 and an S&S CIF filter to collect particles and any ammonium sulfate or semi-volatile organic material lost from the particles during sampling. An active blank system with a filter at the inlet is used to correct for any inefficiency in the denuder and dryer for the removal of gas phase material.

RESULTS

The RAMS blank corrected data are illustrated in Figure 1 for both Philadelphia and Atlanta. Also shown in Figure 1 are conventional TEOM monitor data for the same time periods. As indicated, the concentrations of PM_{2.5} measured by the RAMS is generally either equal to or greater than that measured by the TEOM monitor. The time periods where greater PM_{2.5} mass is measured by the RAMS are those when measurable concentrations of semi-volatile material (dominated by semi-volatile organic material) are measured by the RAMS, but not the TEOM monitor.

The results obtained for the continuous determination of PM_{2.5} with the RAMS have been validated by comparison with results obtained from the PC-BOSS integrated samples to determine the mass of fine particulate material retained on a filter⁵ and the semi-volatile organic material and ammonium nitrate lost from the filter during sampling with a PC-BOSS⁵. Results obtained with RAMS and PC-BOSS denuder sampler show that PM_{2.5} mass, including semi-volatile fine particulate nitrate and organic species can be continuously and accurately monitored with the RAMS. The linear regression of RAMS vs PC-BOSS results give a slope of 1.02 \pm 06 (n=7) for the Philadelphia data and comparable results for Atlanta. The average composition of the fine particles collected during the time period shown in Figure 1 at Philadelphia is shown in

Figure 2. As indicated, an average of 35% of the $PM_{2.5}$ was lost from particles during sampling at Philadelphia. These species were not measured by either the TEOM monitor or a single filter sampler. The results obtained at Atlanta were similar, Figure 1.

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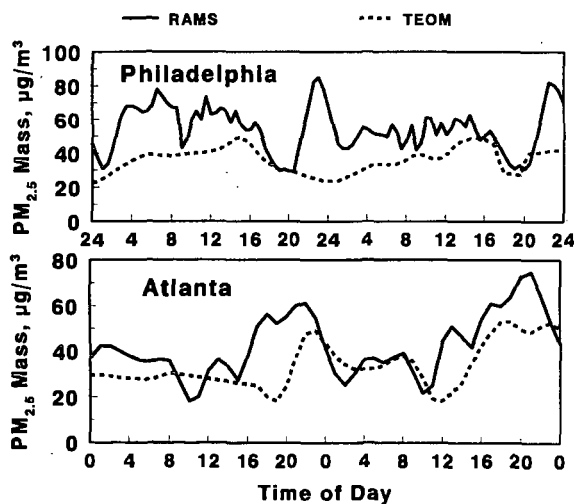


Figure 1. Comparison of 2 h running average of RAMS and TEOM monitor data at Philadelphia. The higher mass measurements with the RAMS is due to the determination of semi-volatile fine particulate material.

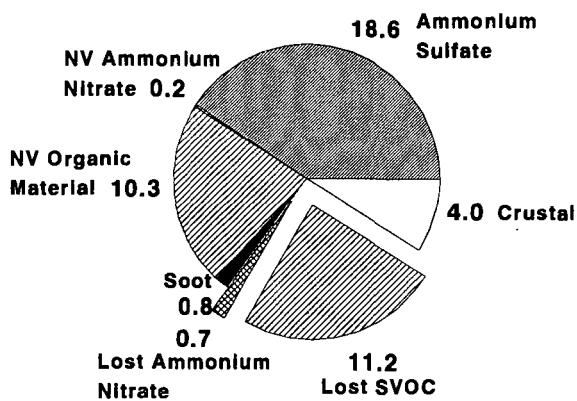


Figure 2. Composition of Philadelphia $PM_{2.5}$. The ammonium nitrate and SVOC lost from particles during sampling are collected by the RAMS, but not a TEOM monitor.